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Volume 1. Petroleum
Wastewater Pond Bottoms

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LAND TREATMENT FIELD STUDIES

Volume 1. Petroleum Wastewater Pond Bottoms

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Contract No. 68-03-2602

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This report presents the results of field measurements and observations on a land treatment site for management of waste bottoms from a petroleum wastewater treatment pond. The waste is typically 13% solids, 25% oil, and 62% water as spread. The site was sampled twice, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analyses were performed on plant samples.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations on a land treatment site for management of waste bottoms from a petroleum wastewater treatment pond. The waste is typically 13% solids, 25% oil, and 62% water as spread. The site was sampled twice, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analyses were performed on plant samples.

The site is a 20-acre portion of land in the western region of the United States which was selected specifically for the experimental land treatment of the generator's petroleum refining wastewater treatment pond bottoms. The geophysical characteristics (topography, meteorology, hydrology, etc.) of the site pose no significant concerns regarding possible contamination of the surrounding environment.

Management methods include monitoring of the soil, waste, and an experimental alfalfa crop, and recording waste application information. Waste is infrequently applied at the site (once a year at most). Applications occurred in 1973, 1974, 1978 and 1979. No commercial crops were grown on the site, but an experimental crop of alfalfa was grown in 1974 on the 1973/1974 application area. The waste generator has applied fertilizers (urea and phosphate) on an experimental basis to optimize the carbon/nitrogen ratio for microbial degradation of wastes.

Significant increases in soil concentrations for several heavy metals were predicted and measured. Measurements also indicated that organic wastes were being biodegraded. Sodium levels in alfalfa plants grown in the application area were greater than those in alfalfa plants grown in the control area. This increase might have been due to subsurface saline seeps in the area, however.

This report was submitted in fulfillment of Contract No. 68-03-2602 by Arthur D. Little, Inc., under sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1977 through February 1981 and work was completed as of May 1981.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii

1. Introduction 1
   Objectives 1
   Description 2
2. Conclusions and Recommendations 8
3. Approach 10
   Data Collection and Analysis 10
   Data Interpretation 10
4. Results and Discussion 17
   Waste Characteristics 17
   Soil Characteristics 21
   Plant Analysis 32

Appendix, Methods of Sampling and Analysis 36

FIGURES

Number		Page
1.	LC Results for CTL Samples	25
2.	R + DB Clusters for CTL 0-6 Samples	26
3.	R + DB Clusters for CTL 6-12 Samples	27
4.	Schematic Representation of LC Separation into Aliphatic (H), Aromatic (A) and Polar (X) Organic Classes	28
5.	R + DB Cluster Profiles, Relative Abundance Basis	30
6.	Flow Chart of Proposed Organic Analysis Scheme	38
7.	Example of Display of R + DB and Elemental Composition Groupings for a Soil Sample Extract	43

TABLES

Number		Page
1.	Selected Physical/Chemical Characteristics of the Site	3
2.	Operational Management for the Site	6
3.	Comparison of "Typical" Elemental Concentration Ranges in Soils and Plants with Corresponding Concentration Ranges in Control Areas used in this Study	10
4.	Inorganic Waste Analysis and Predicted Years for Observable and Concentration Increase	17
5.	R + DB Summary Matrix for Site Waste Sample	19
6.	Inorganic Analysis of Control and Application Soils	21
7.	Site Soils: Inorganic Parameters	22
8.	Quantities of Total and Extractable Organic Material in Control Soil Samples	24
9.	Plant Sample Content of Total Elements as Analyzed in Ashed Samples for Site D	32
10.	Soil Samples: DTPA Extractable Metals for the Site	34
11.	Replicate Extractions and LC Separations on a Site Soil Sample	41

SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semisolid waste into surficial soils. Other terms used to describe this practice include land farming, land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition, attenuation and migration of waste constituents. The extent to which any one of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a land treatment site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a buildup of total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussion , it is evident that specific site characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not as evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVES

The objective of this project was to identify parameters which contribute to (or affect) the environmental acceptability of landfarming a wastewater treatment sludge from the petroleum refining industry on a dedicated site. The parameters are classified by waste characteristics (e.g. percent solids, salt content), site characteristics (e.g., topography, climate) and landfarm management procedures (e.g., soil aeration, frequency of waste application). Environmental acceptability was determined by significant increases in waste constituents in the application soils compared to controls and by the potential for environmental contamination due to a combination of waste, site and management parameters.

DESCRIPTION OF THE SITE

The identity of the site is protected by a confidentiality agreement included as part of the contract for this study. The site is located in the western range region of the United States and was set aside specifically for the experimental land treatment of petroleum refining wastewater treatment pond bottoms.

Waste Characteristics

The waste landfarmed at this site represents sludges from wastewater holding ponds for petroleum refining wastes (SIC Code 2911). Land treatment of these wastes was considered an attractive option when it was no longer possible to dispose of these wastes at a local landfill. The waste consists of oily solids which collect in the aerated wastewater holding pond. The solids are removed to storage pits which are periodically cleaned and are sent to land treatment. The sludge is typically 13% solids, 25% oil and 62% water as spread.

Site Characteristics

The site was chosen over a number of other potential sites after a long search because it met the criteria of the site personnel. These criteria included isolation of the site from populated areas, relatively flat terrain, and a suitable distance from drinking water, both ground and surface.

Table 1 lists the published and observed physical/chemical characteristics of the site. Surface soils are clay-like in nature and their depth to bedrock varies from 25.5 cm to greater than 150 cm. The soils are also saline, and although "surface seeps"* were not observed on the application areas, they did exist beneath the soil surface within the area boundaries. These soils are slowly permeable, and have limited vegetative cover. Given these conditions and the lack of substantial precipitation in this region, both wind and surface runoff erosion into a nearby stream are a potential problem. Berms have been constructed to control the latter.

No test wells have been developed at this site. Thus, identification of groundwater location is not certain. In general, this region does not have an abundance of groundwater supplies. In the immediate vicinity of the site, facility personnel indicated there were no potable groundwater supplies (for human use). The region typically produces water of sufficiently good quality for livestock use, which does occur adjacent to this site. It is worth noting that most groundwater obtained in this region is not suitable for large-scale irrigation, both because of the typically clay-like soil of the area and the dissolved solids levels in groundwater (a situation confirmed by facility personnel). Based on the information gathered in this study, there is nothing to indicate a potential for direct contact between applied waste and groundwater.

---

*Seeps are places where soil water comes to the surface, such as a puddle or spring. In saline soils, they can be identified by the salt deposits left on the soil surface.

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

	Published source*	Data from site visit/analysis**
I. Soil Conditions		
A. Soil classification	Ranges from deep, moderately well drained, fine textured silty clay loam to shallow, silty clay	"Bentonitic Clay" subsurface saline seeps
B. pH characteristics	7.4-9.2	7.8-7.9
C. Cation exchange capacity (meq/100g soil)	-	26.9 to 28.5 meq/100g (control area)
D. Soil organic content (or TOC)	Low-moderate	TOC: 0.63% dry solids (control area)
E. Water retention ability	a) Available water capacity: 0.14 to 0.16 inches per inch of soil b) Permeability: <0.06 to 0.20 inches per hour	-
II. Ground & Surface Water Proximity		
A. Surface Water	Intermittent stream along northeast border of site	Stream is very high in dissolved solids; 20,000 to >40,000 ppm TDS
B. Ground water	Depth for wells in coulees ≤35'; drilled wells <200'; quality and quantity quite variable (could be brackish)	Lack of usable water for this operation noted
III. Topographic Conditions		
A. General topography of vicinity of site	Hilly; 0 to 4% slopes and 15 to 35% slopes	-
B. Topographic relief of area visited	-	Application areas nearly flat, other portions of site 5 to 10% slopes.

(Continued)

TABLE 1. (Continued)

	Published Source*	Data from site visit/analysis**
IV. Meteorological Conditions		
Average yearly precipitation	28-35 cm	
Typical distribution of Ppt***	~70% average growing season	
Frost free period	~120-125 days	
Average temperatures		
summer maximum (°C)	31	
winter minimum (°C)	- 12	

* Includes information from Soil Conservation Service Personnel & publications, USGS Surveys and/or state and university surveys.

** Includes Arthur D. Little, Inc. observations and analyses from site visits, as well as interviews with facility personnel and representatives of waste generator.

*** This figure represents a 30-year average; facility personnel have indicated that as little as 45% of the yearly precipitation can fall during the growing season.

The alkaline pH, high clay content, high cation exchange capacity and low precipitation levels make the likelihood of groundwater contamination low. More probably metal attenuation and accumulation of organics may occur. The latter condition is possible because of the reduced aeration potential of the compacted soils, limited rainfall and the cool climate, all of which are limitations to microbial degradation.

The 20-acre land treatment site is immediately surrounded by grazing land presently in use. Tilled fields are located in close proximity and two residences exist within a 1.5 mile radius. The site had been used for growing winter wheat, but with its low fertility, the previous owner had been unable to recover seed costs. Some alfalfa has been planted as an experimental crop in the area of waste application, but most of the site is covered by agricultural escapes and indigenous weedy vegetation.

There are no plans at present for site closure, although refinery personnel assume that the site could be used for forage crops or for grazing, assuming plant metal-uptake is not excessive. (State regulatory authorities have not, to date, outlined closure requirements, although revegetation of application areas is considered a reasonable assumption.)

The site is accessed from a main road, via four miles of clay/gravel and clay roads which are nearly impassable when rain soaked. The site itself is surrounded by a 6-foot cyclone fence, and thus is not accessible (except if vandalized) to local residents or cattle. Natural buffer areas do not exist; trees are rare in the region. Berms or dikes have been constructed around six plots, each less than two acres, to protect against runoff in a hundred year storm. The general appearance of the site is much like that of the surrounding area.

Fauna known to utilize the land treatment site include insects, large lizards, and a regionally representative variety of birds, including killdeer, meadowlark, sparrows, predatory birds, and reportedly, sage grouse. Antelope were observed in the areas immediately adjacent to the site. There is no reason to believe that any of the other fauna typical of the region, including such species as coyote, rabbit, deer mice, and prairie dogs, are absent from the site vicinity. In fact, some or all could use the site itself.

Land Treatment Site Management

Waste disposal activities at the site are carried out infrequently; applications occurred on the site in 1973, 1974, 1978 and 1979. The 1978 application consisted of 68,000 gallons of sludge spread over 1.7 acres. Since application of the waste occurs at most once a year, virtually all operations have been carried out by contractors, with the waste generator participating where needed. (Table 2). Personnel under the employment of the waste generator spend approximately ten man days per year supervising land treatment activity and sampling.

Contract haulers transport and apply the waste; the vehicle is a tank truck, which permits waste application by gravity flow. At the beginning of the application path, a considerable amount of sludge is deposited because the driver must open the valve before re-entering the truck cab. The rate of sludge

TABLE 2. OPERATIONAL MANAGEMENT FOR THE SITE

Function	Person who Plans/Decides Management/Supervises	Person who Performs	Person who Approves/Checks
Storage	W.G.	W.G.	W.G.
Pretreatment	W.G.	W.G.	W.G.
Waste Mixing	None		
Transport	W.G.	C.H.	W.G.
Application	W.G.	C.H.	W.G.
Soil Incorporation	W.G.	C	W.G.
Soil-Waste-Amendments	W.G.	W.G./C	W.G.
Farming	None		
Monitoring	W.G.	W.G.	W.G.

W.G. = Waste Generator/Site Owner
C.H. = Contract Hauler
C = Contractor

applied per unit surface area varies with the speed of the truck and with the amount of storage in the truck.

The amount of sludge/unit area is generally three to four inches high. After a several week drying period at which time the height of the sludge layer should be about 1" thick, a contractor roto-tills the waste into the top five to six inches of soil. Following the 1973 application of waste, the site was roto-tilled twice a month; this practice was discontinued when the soil became extremely dry due to a hot, dry summer.

Fertilizers (urea and phosphate) have been applied on an experimental basis to try to optimize the carbon/nitrogen ratio for microbial degradation of the waste. Monitoring was carried out on a voluntary basis in 1973 and 1974 for extractable oil, water, solids, TOC and metals in the waste and for oil content in the soil. The soil samples were analyzed for indications of waste degradation rates and classes of organic degradation products. Analysis of an experimental alfalfa crop was also conducted in 1974.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constituents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded for any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the same chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the environmental acceptability of land treatment for wastewater treatment lagoon sludges from one particular petroleum refining plant, at one particular application site. The results cannot be generalized, either to wastewater treatment lagoon sludges from other manufacturing plants in the petroleum refining industry, or to other potential land treatment sites for the particular wastewater treatment lagoon sludge investigaged. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site for purposes of waste treatment rather than for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSION

The waste sludge as applied contained about 13% solids, 25% oil and 62% water. Approximately 68,000 gallons had been applied over a 1.7 acre area in each of the years 1973 and 1974. Alfalfa had been planted on the site following the 1973 application. The field study was conducted in 1978, about four years after the last sludge application.

Analysis of the dried waste solids showed 10% metals, 28% TOC, 2% nitrogen, less than 1% sulfate and chloride, and 60% undetermined. Of the metals analyzed*, chromium, copper, sodium, selenium and zinc were found in significantly higher concentrations in the application area than in the control area. The observed accumulations of the heavy metals in the upper six inches of soil are compared with the assimilative capacity of soils with a high CEC in the following table:

*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

Metal	Observed Accumulation (kg/ha)	Assimilative Capacity CEC 15 (kg/ha)†
Cr	275	500
Cu	78	500
Se	3	9
Zn	325	1000

In every case, observed soil accumulation is below the cumulative limits.

Sodium was higher in the application area than in the control area, and also higher at the 6-12 inch soil depth than at the 0-6 inch depth. Increases in electrical conductivity, sulfate and chloride in the application area compared to the control area follow the same pattern as sodium. These results may be due to leaching of soluble sodium salts or to a saline seep reported by site personnel to underlie a portion of the area sampled.

Extractable organics were found at significantly higher concentrations in the application area than in the control area, 3000 mg/kg vs 140 mg/kg in the upper six inches of soil. The application area soils were also much richer in polar organics (particularly C, H, O compounds) than the waste, indicating that some oxidation degradation was occurring. However, significant accumulation of non-oxigenated aliphatic and aromatic hydrocarbons was also noted.

Alfalfa grown on the application site had significantly higher concentrations of calcium, copper, potassium, molybdenum, sodium, phosphorous and vanadium than alfalfa grown on the control site.

RECOMMENDATIONS

The land treatment operation is an experimental site for the disposal of petroleum refining wastewater treatment pond bottoms. This site provides an excellent opportunity to study organic degradation rates, heavy metal attenuation, and plant uptake. More controlled studies of plant uptake of pollutants should be conducted as this information will be important for post closure considerations.

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†M. Overcash and D. Pal, "Design of Land Treatment Systems for Industrial Wastes," Ann Arbor Science, Michigan (1979).

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Element	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-500)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Allaway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six landfarm sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six landfarm sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly. For other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre/year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Leading Rate of Individual Waste Species --

The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --

The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ~1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capabile of detecting a change in concentration

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[The average mass of one acre-foot of soil was calculated as follows:

1 acre $\sim$ 43,560 ft^3; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) 2 x 10^3 kg
Therefore,
(mg/acre-foot/yr) $\simeq$ 2 x 10^6 kg/acre-foot = $\frac{\text{mg of element of interest}}{\text{kg of soil-year}}$ = ppm/year]

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be $\sim$ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \simeq 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION 4

RESULTS AND DISCUSSION

WASTE CHARACTERISTICS

Total Mass of Parameters

The percent of dried solids analyzed in the waste was 40.4%, and is broken down as follows:

	%*
Metals	10.06
TOC	28.24
N	2.08
SO_4	0.02
Cl	0.002
	40.4

* % of dried solids

Species not determined include Fe, H, O, Si, and Al.

Elemental and Inorganic Analysis

The results of analysis for total metals, TOC and TKN in the waste are presented in Table 4 below. These data were used along with data obtained from the site owner on waste application rate and % solids, to calculate an estimate of the years of waste application necessary before one could expect to observe any increase above background in the application area soils of the elements in Table 4. At this site in particular, the exact composition of wastes sampled in 1978 and described in Table 4 may differ somewhat from the wastes applied in 1974 to the landfarm areas sampled. Based on the above, observable increases of elements in the soil at the time of sampling might be expected for C, P, Na, Ca, Cr, N, Se, As, K, Mg and Zn (in decreasing order of predicted concentration). Table 4 illustrates this prediction.

Although some of the assumptions for this calculation clearly do not hold in this case, it is believed useful as a reference point for considering the reasonableness of soil analysis results and helping interpret these results.

TABLE 4. INORGANIC WASTE ANALYSIS AND PREDICTED YEARS FOR OBSERVABLE CONCENTRATION INCREASES

Element	Concentration (mg/g dry wt.)	Estimated years of waste application necessary for predicted observable concentration change in soil
As	105	1
B	39	*
C	28.24%	1
Ca	1.5%	1
Cd	9.6	*
Cr	1.3%	1
Cu	310	*
K	7900	1
Mg	5400	1
Mo	22	*
N	2.58%	1
Na	2.1%	1
Ni	19	*
P	3.1%	1
Pb	89	*
Sc	150	1
V	39	*
Zn	6500	1

* = greater than 10 years

Organic Analysis

The 1978 waste was a slurry that was found to contain 1100 mg/L (0.11%) of extractable organics. Because of severe emulsion problems encountered in the extraction of this sample, the level of extractable organics may have been underestimated. However, the measured 0.11% value is consistent, within a factor of 2, with the measured TOC of the solid portion of the waste (the waste as sampled was about 1% solids which had a TOC of 28.24%). On the basis of LC separation of the extract, the organic materials could be characterized as follows:

Aliphatic Hydrocarbons, non-volatile (GRAV):	41%
volatile (TCO)	39%
Aromatic Hydrocarbons, non-volatile (GRAV):	10%
volatile (TCO):	3%
Polar Organics, non-volatile (GRAV):	7%

The recovery from the LC column for this sample was 101%. The presence of >40% by weight of TCO-range organics is significant in that those materials can potentially undergo evaporative transport from soil to air, in addition to possible degradation in the soil.

Facility personnel, however, had concluded that evaporative losses were not significant, based on their monitoring of soil organics following the 1973/1974 applications, but it is not clear that their procedures would have been adequate for detection of the TCO-range organics most likely to be volatilized.

The results of the HRMS analysis of the waste extract are presented in the R + DB summary matrix (Table 5). The waste was found to contain a variety of aromatic hydrocarbons (R + DB 4), including polynuclear aromatic hydrocarbons (PAH's) with three (R + DB 10) to six (R + DB 19) fuxed rings. The waste extract also contains rather small quantities of oxygen- and nitrogen-containing species and somewhat larger amounts of sulfur-containing species. The oxygenates are mainly R + DB 0-4 species which are found, from the ELCOMP data, to contain only one oxygen atom each. There is also evidence for the possible presences of dibenzofurans (R + DB 9). The most abundant C,H,N category is R + DB 9, which includes the carbazoles. Aromatic sulfur species whose presence is inferred are benzothiophenes (R + DB 6) and dibenzothiophenes (R + DB 9), among others.

Considered as a whole, the HRMS R + DB matrix analysis results are very similar to those that had previously been obtained for an API separator bottom extract (Table 5) from another source, and confirm the petroleum-based origin of the site waste stream. The similarity between the two wastes from different refinery sources suggests that both are examples of a "typical" qualitative organic composition for petroleum derived oily sludges. This, in turn, increases confidence that the waste sampled in 1978 may be a reasonably good model for the organic composition of wastes applied in 1973 and 1974.

TABLE 5. R + DB SUMMARY MATRIX FOR SITE WASTE SAMPLE*

R + DB	C,H	C,H,N	C,H,O	C,H,S
0				0.6
1	10.3		.4	.3
2	8.9		.6	
3	0.0	.1	.2	.5
4	10.2		.2	.7
5	6.5		.1	.3
6	5.1		.1	1.3
7	5.3	.1		.6
8	4.0		.1	.6
9	3.9	.4	.9	3.9
10	4.9		.3	1.8
11	4.6	.1		1.1
12	3.6		.3	1.3
13	1.7		.1	.4
14	2.9			.2
15	.7			
16	.2			.1
17	.3			
18	.1			

*All values in %, normalized to 100%

SOIL CHARACTERISTICS

Wastes had been applied to the test plot soils in 1973 and 1974. Soil and plant samples were collected on September 11, 1978.

Inorganic Analysis

Inorganic analytical data on soils are presented in Table 6. As previously discussed, for the purpose of this report, it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than ±20% relative to the mean CTL area concentration (i.e. APN/CTL >1.2 or the ratios of total concentration in application area to total concentration in control area). "APN/CTL ratios" are shown in Table 6 for total metals, total organic carbon (TOC), and total Kjeldahl nitrogen (TKN).

Based on calculations, concentration increases were predicted for chromium, selenium, sodium, carbon, copper, and zinc (listed in decreasing order). Increases were observed for sodium, carbon, chromium, zinc, copper and selenium (listed in decreasing order). No increases were observed which were not predicted.

The observed concentration increases for C, Cr, Se, and Zn are all less than predicted, while that for Cu is greater than predicted. However, the absolute differences between calculated and observed concentration changes in all cases are small, and in any case comparison of the waste and the application area sampled in this study should be viewed with caution, since the waste last applied to that application area prior to this sampling visit was, according to site personnel, quite likely to be different in chemical composition than the waste sampled in this study. Increases in the concentrations of Ca, K, and Na in the APN 6-12 samples relative to the APN 0-6" samples may be due to a saline seep which is reported by site personnel to exist under a portion of the application area sampled in this study.

Data for pH, CEC, sulfate, chloride, and electrical conductivity are given in Table 7. The significant increases in APN area samples of electrical conductivity, $SO_4^=$ and Cl^- suggest that Na, K and Ca may be present in some combination of soluble chlorides and sulfates which are either being leached downward below the zone of incorporation or are due to the saline seep reported by facility personnel to be presented below application area soils.

Organic Analysis

Control Area Soils--

Control samples were collected from five land treatment sites, consisting of composite 0-6" and composite 6-12". Soil cores from each site were analyzed to characterize the extractable organic materials that might be found in a range of natural soils. This characterization is important because of the difficulty in establishing control areas in terms of extractable organics, a "typical" control soil sample contains <150 mg/kg of extractable organic material, all in the GRAV range, that is polar (>80% in LC-X. The HRMS matrix analysis approach shows

TABLE 6. INORGANIC ANALYSIS OF CONTROL AND APPLICATION SOILS

Element	Concentration in Soils (µg/g) dry wt.				
	CTL		APN		APN/CTL*
	0-6"	6-12"	0-6"	6-12"	
As	6	8	7	7	1.0
B	9.2	12	4.7	10	.7
TOC	0.63%	NA	1.04%	NA	1.7
Ca	8600	8300	4300	8400	0.8
Cd	0.7	0.7	0.7	0.7	1.0
Cr	7.9	8.6	110	15	7.6
Cu	15	17	31	17	1.5
K	5600	7600	5000	9700	1.1
Mg	4900	5300	5000	5000	1.0
Mo	3.0	3.0	2.3	3.0	0.9
TKN	760	NA	812	NA	1.1
Na	360	530	1200	4000	5.8
Ni	20	21	19	20	1.0
P	8500	8700	8100	8200	0.9
Pb	28	27	37	28	1.2
Se	0.1	0.1	1.1	0.3	7.0
V	40	53	33	44	0.8
Zn	82	86	130	84	1.3

NA = Not analyzed
* - APN/CTL Ratio calculated as $\left\{ APN(0\text{-}6) + APN\ (6\text{-}12) \right\} \Big/ \left\{ CTL(0\text{-}6) + CTL(6\text{-}12) \right\}$

TABLE 7. SITE SOILS: INORGANIC PARAMETERS

Sample	pH	C.E.C. meq/100g	E.C. µmhos	$SO_4^=$ µg/g	Cl µg/g
Waste				200	17
Soil:					
CTL 0-6	7.9	28.5	1010	520	0.1
CTL 6-12	7.8	26.9	1340	600	0.6
APN 0-6	7.9	19.9	2400	1300	12
APN 6-12	8.2	21.5	8500	5300	68

predominantly R + DB 1-4 hydrocarbons and oxygenates, with some R & DB 5-9 hydrocarbons and nitrogeneous materials. Little or no material in the R & DB 10 range was present.

This definition of a typical control sample constitutes one general fixed reference point for evaluation of data on application area soil samples. The other reference point is the waste applied to the landfarming site.

Table 8 presents data on the total organic carbon content and the quantity of extractable organic material in control soil samples. Figures 1-3 illustrate the results of the LC separation and HRMS analysis. It is obvious that a small and highly variable portion of the soil organic material is extracted by methylene chloride. Known types of non-extractable organics include high molecular weight polymeric materials, such as amino acids. Non-polar and moderately polar organic species of molecular weights up to 500 or 1000 are generally efficiently extracted from environmental samples by methylene chloride. All of the extracted material is in the GRAV range (b.p. >300°C) which is expected, since TCO range organics (b.p. 100-300°C) would be lost from soil by volatilization. Also expected is the observation that CTL 6"-12" samples have considerable lower levels of extractable organics than CTL 0"-6" samples.

Application Area Soils --

The 1973/74 application area 0-6" depth (APN 0-6) and 6-12" depth (APN 6-12) samples were found to contain 3000 mg/kg and 520 mg/kg, respectively, of extractable organic material. These values are substantially higher than the corresponding levels for the control samples of 140 mg/kg for CTL 0-6 and 89 mg/kg for CTL 6-12. These data imply that there has been a significant accumulation of extractable organic materials in the waste application area soil samples.

Figure 4 presents the results of the LC separation of the site application area samples, as well as those of the corresponding waste and control area samples. Comparison of the APN 0-6 and waste sample extract results reveals that the APN 0-6 sample is relatively much richer in polar organics (LC-X = 34% of total) than is the waste (LC-X = 7% of the total). The enrichment of polar materials is even larger in the APN 6-12 sample (47% LC-X). This shift in distribution towards polar materials is what would be expected to occur as a result of oxidative degradation of waste components in the soil. On the other hand, aliphatic (LC-H) and aromatic (LC-A) hydrocarbons account for more than 50% of the organics in both the APN 0-6 and APN 6-12 sample extracts. Since LC-H and LC-A contribute <10% of the CTL 0-6 and 6-12 sample organics, this implies that a substantial quantity of LC-H and LC-A material from the waste has remained in the soil without undergoing oxidative degradation.

Compared to the 1978 waste sample, the older APN 0-6 sample is very much depleted in volatile (TCO) aliphatic and aromatic hydrocarbons (59% of APN 0-6 vs. 42% of waste). The waste generator believes that volatilization is not an important process in the disposal operation. Examination of the LC-H and LC-A data for the non-volatile (GRAV) materials shows some evidence for selective

TABLE 8. QUANTITIES OF TOTAL AND EXTRACTABLE ORGANIC MATERIAL IN CONTROL SOIL SAMPLES

	Organic Material mg/kg	
	Total organic carbon	Extractable organic
CTL 0-6"	6,300	145
CTL 6-12"		89

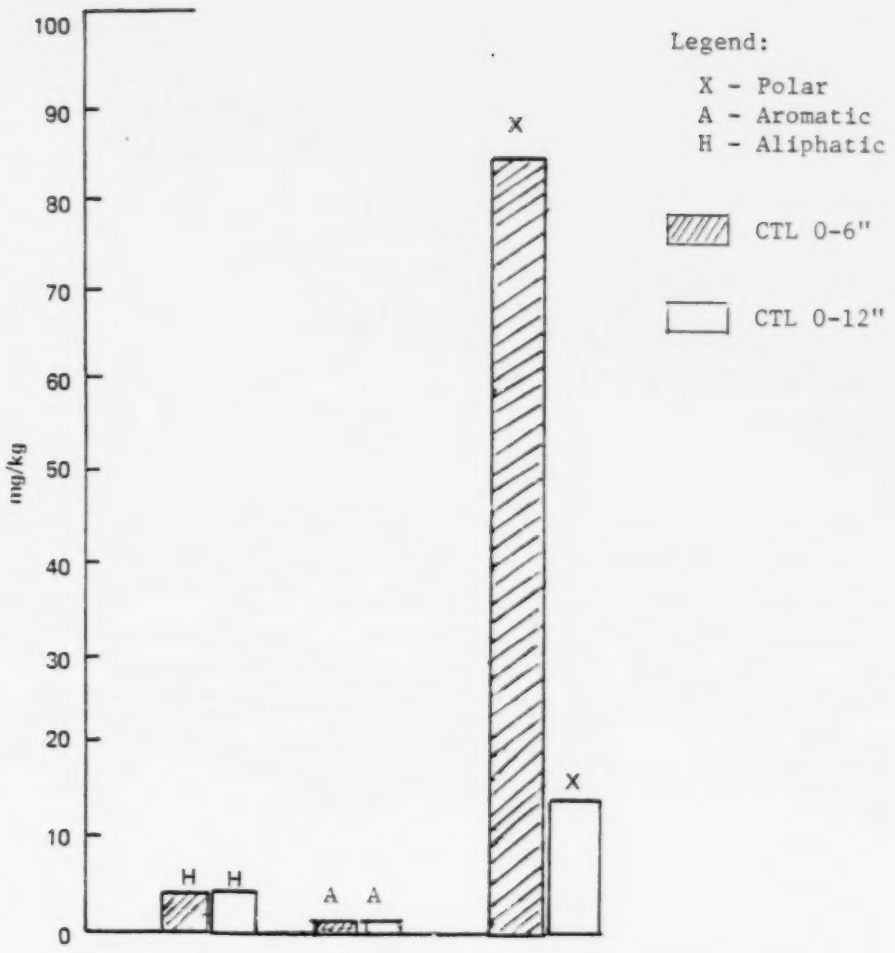

Figure 1. LC REsults for CTL Samples

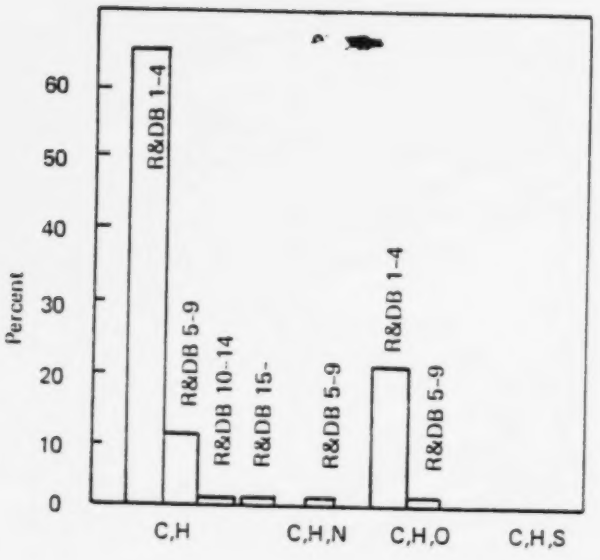

Figure 2. R + DB Clusters for CTL 0-6 Samples

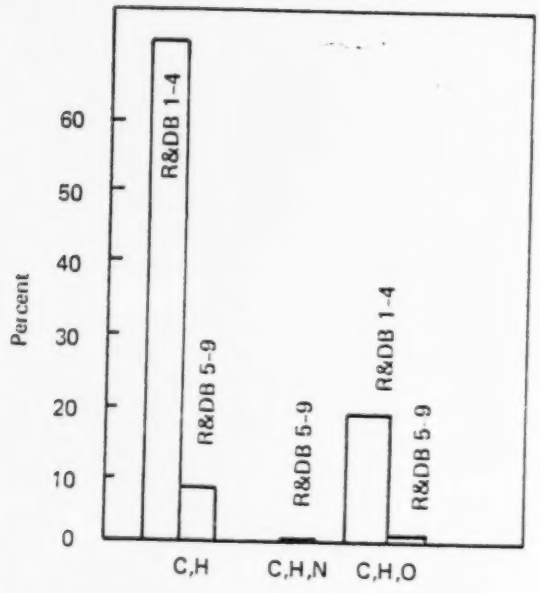

Figure 3. R + DB Clusters for CTL 6-12 Samples

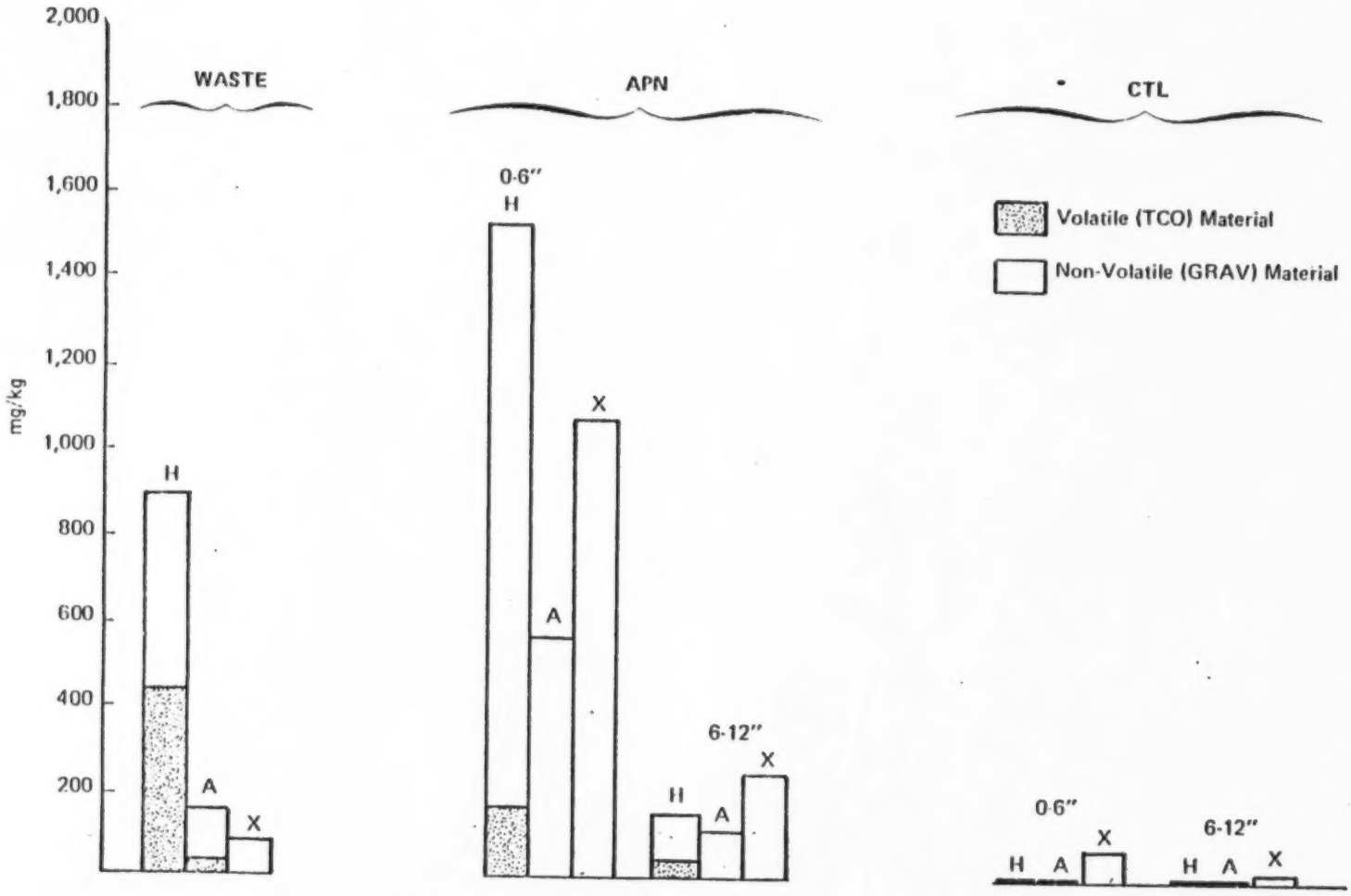

Figure 4. Schematic Representation of LC Separation Into Aliphatic (H), Aromatic (A) and Polar (X) Organic Classes.

degradation/accumulation of the waste components. In the waste itself, LC-H constitutes 70% of the GRAV range material and the ratio of LC-A to LC-H is 0.24. In the APN 0-6 sample, LC-H constitutes 46% of the GRAV material, and the ratio of LC-A to LC-H GRAV values is 0.37. In the APN 6-12 sample, corresponding values are 25% and a ratio of 0.96. The data imply that preferential loss/degradation of aliphatics and/or preferential accumulation of aromatics is occurring.

In Figure 5, the R + DB cluster profiles, on a relative distribution basis, are plotted for the waste, APN 0-6, APN 6-12 and CTL 0-6 samples. Examination of the data in this form reveals that there is little apparent change in the hydrocarbon distribution among R + DB clusters 1-4, 5-9, etc. There is therefore no strong evidence for selective degradation or accumulation of any particular class of unsaturated hydrocarbons compared to any other. In particular, there does not appear to be selective enrichment in the soil of the three-, four-, five- and six-ring PAH compared to the lower analogs. There is in fact an indication in the data that the R + DB >10 hydrocarbons are relatively less abundant in the APN samples than in the waste, but the differences are not large enough to attribute great significance to them without further confirmation.

The R + DB cluster profiles for heteroelement compositions (Figures 2 and 3) imply that C, H, O, R + DB 0-4 moieties are major contributors to the abundant polar organic fraction of APN 0-6. Based on the ELCOMP data, the increase in this R + DB category correlates with an increase in the abundance of $C_xH_yO_2$ and $C_xH_yO_3$ ions in the HRMS. The species present in APN area samples appear to be fragment ions (3-10 carbon atoms) of fatty acid/ester materials. These are also the types of ions found (at much lower levels) in control samples and may be taken as positive evidence of biodegradation of waste components in the soil. In the R + DB 5-9 cluster, the most abundant APN 0-6 area components appear, based on ELCOMP, to be a series of benzofurans (R + DB 6), which were not major 1978 waste components. The data cannot establish whether the benzofurans might derive from the dibenzofurans (R + DB 9), indicated by ELCOMP as major components of the R + DB 5-9, C,H,O cluster in the waste. The application area samples also contain significant quantities (>15 mg/kg) of oxygenated materials in higher R + DB categories (R + DB 10-20). These compounds, generally not present in the 1978 waste, are mono-oxygenated based on ELCOMP data, and probably represent the initial products of stepwise oxidation of PAH components in the waste. It is not possible to determine from ELCOMP whether these are keto-, epoxy-, or hydroxy-PAH's.

Figure 5 shows evidence for some accumulation of C,H,N species in the APN 0-6 sample. The C,H,N species are in very low relative abundance (>1%) in both waste and APN 0-6. The APN 0-6 C,H,N materials identified by ELCOMP are relatively low molecular weight species such as quinolines (R + DB 7) and are probably fragment ions from higher molecular weight species. The major waste C,H,N components appeared to be a carbazole series (R + DB 9). It is not reasonable, based on the available data, to speculate on the existence or nature of possible soil processes concerning these materials.

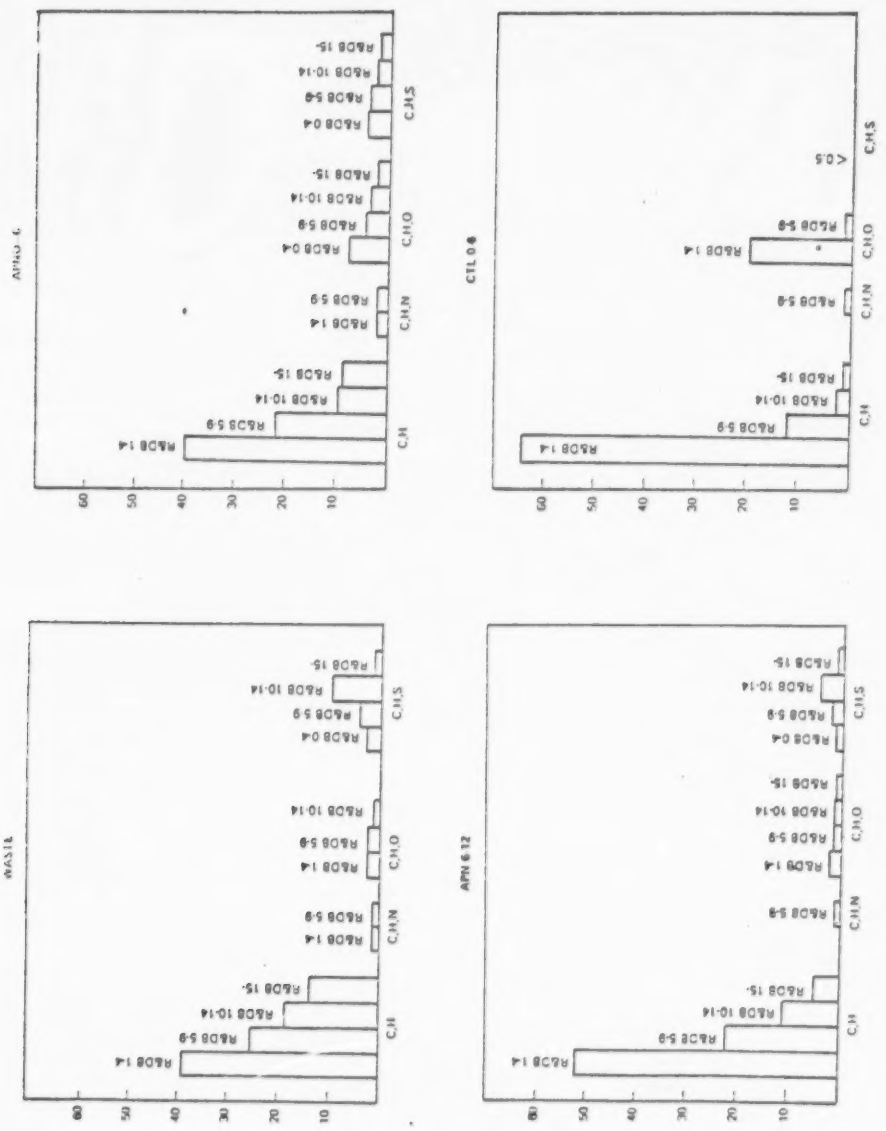

Figure 5. R 4 DB Cluster Profiles, Relative Abundance Basis

The HRMS data also indicate elevated levels of C,H,S species in the APN 0-6 and APN 6-12 samples. There appears to be a substantial difference in distribution towards lower R + DB groups in APN 0-6 compared to the waste. The ELCOMP data show no differences in elemental composition between the abundant R + DB 0-4 C,H,S ions in APN 0-6 and the relatively sparse R + DB 0-4 C,H,S ions in the waste. These are apparently all ms fragment ions ($\leq C_6$). The elemental compositions of C,H,S ions in R + DB 5-9, 10-14 and 15- in APN 0-6 and 6-12 are also very similar to those found in the waste. It is therefore not possible to use the ELCOMP data to try to interpret the differences in the C,H,S cluster profiles, except to note that some observable differences between waste and APN samples exist. The existence of these differences implies that some transformations of the C,H,S waste components may be occurring.

Based on the above results one can make the following observations about the accumulation and degradation of organic waste components at the site landfarm:

1. Extractable organic material has accumulated in the application area.

2. An enrichment in polar material, especially oxygenates, indicates that oxidative degradation of waste components has occurred.

3. Some aliphatic and aromatic hydrocarbons have accumulated without undergoing oxidation.

4. Volatile aliphatic and aromatic hydrocarbons have been preferentially lost from the application area.

5. Non-volatile hydrocarbons show a higher aromatic to aliphatic ratio in the 1973/74 APN samples than in the 1973 waste. However, high molecular weight PAH's do not appear to be selectively enriched in soil compared to lower molecular weight, non-volatile aromatics.

6. Some accumulation of organic nitrogen compounds has occurred.

7. Organic sulfur species have accumulated and appear to have undergone some unidentified transformation processes.

Plant Analysis

Alfalfa samples were collected randomly from the same sampling areas designated for soil samples. Above-ground portions of plants were collected and composited for the application area and the control area, and data for total metals in alfalfa samples collected from the CTL and APN areas are given in Table 9.

TABLE 9. PLANT SAMPLE CONTENT OF TOTAL ELEMENTS AS ANALYZED IN ASHED ALFALFA SAMPLES (all values in μg/g unless noted otherwise)

	% Ash	Elements Analyzed															
		As	B	Ca	Cd	Cr	Cu	K	Mg	Mo	Na	Ni	P	Pb	Se	V	Zn
Alfalfa																	
CTL	9.4	3	620	13.6%	4	34	130	3.6%	4.0%	64	8400	26	1.9%	120	<.8	15	900
APN	9.6	2	570	17.0%	4	38	170	5.0%	3.4%	110	1.5%	22	2.7%	130	<.6	29	990
APN/CTL		0.6	0.9	1.25	1.0	1.1	1.3	1.4	0.8	1.7	1.8	0.8	1.4	1.1	0.7	1.9	1.1

The greatest differences between application and control areas in terms of plant uptake were found for molybdenum, sodium and vanadium (Table 9). Smaller differences were observed for copper and lead, with plant uptake of chromium being very little different at the control and application areas. Data for extractable metals from soils in the two areas (Table 10) do indicate increased sodium, slightly increased vanadium, lead and copper, in the application area. Again, Na levels may be reflective of a reported saline seep in this area. Extractable levels of zinc were also higher in application area soils.

Interestingly, analyses of 1978 waste samples indicate relatively low concentrations of lead and vanadium, modest concentrations of copper, and fairly high concentrations of zinc, chromium, calcium and sodium. Increments in measured soil levels of sodium and chromium are evident in the 1974 application area. While waste levels of arsenic and selenium are present in higher proportions than observed for other wastes examined, and application area soils indicate an enrichment of selenium, application area plants collected were lower in both selenium and arsenic.

TABLE 10. SOIL SAMPLES: DTPA EXTRACTABLE METALS FOR THE SITE (in μg/g)

	Elements Analyzed															
	As	B	Ca	Cd	Cr	Cu	K	Mg	Mo	Na	Ni	P	Pb	Se	V	Zn
CTL 0-6"	NA	0.5	NA	<.1	0.5	2	86	190	<.1	21	2	21	3	NA	0.4	0.9
CTL 6-12"	NA	0.6	NA	<.1	0.1	3	59	210	<.1	52	2	15	2	NA	0.1	0.6
APN 0-6"	NA	0.4	NA	0.1	0.4	7	78	200	<.1	440	2	31	7	NA	0.5	2
APN 6-12"	NA	0.5	NA	<.1	<.1	2	56	280	<.1	1400	2	20	2	NA	0.4	2

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

	Control Area	Application Area
1) Waste	1 Sample	
2) Soil	2 Samples	2 Samples
3) Soil-Waste Mixture	-	2 Samples
4) Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 6. The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

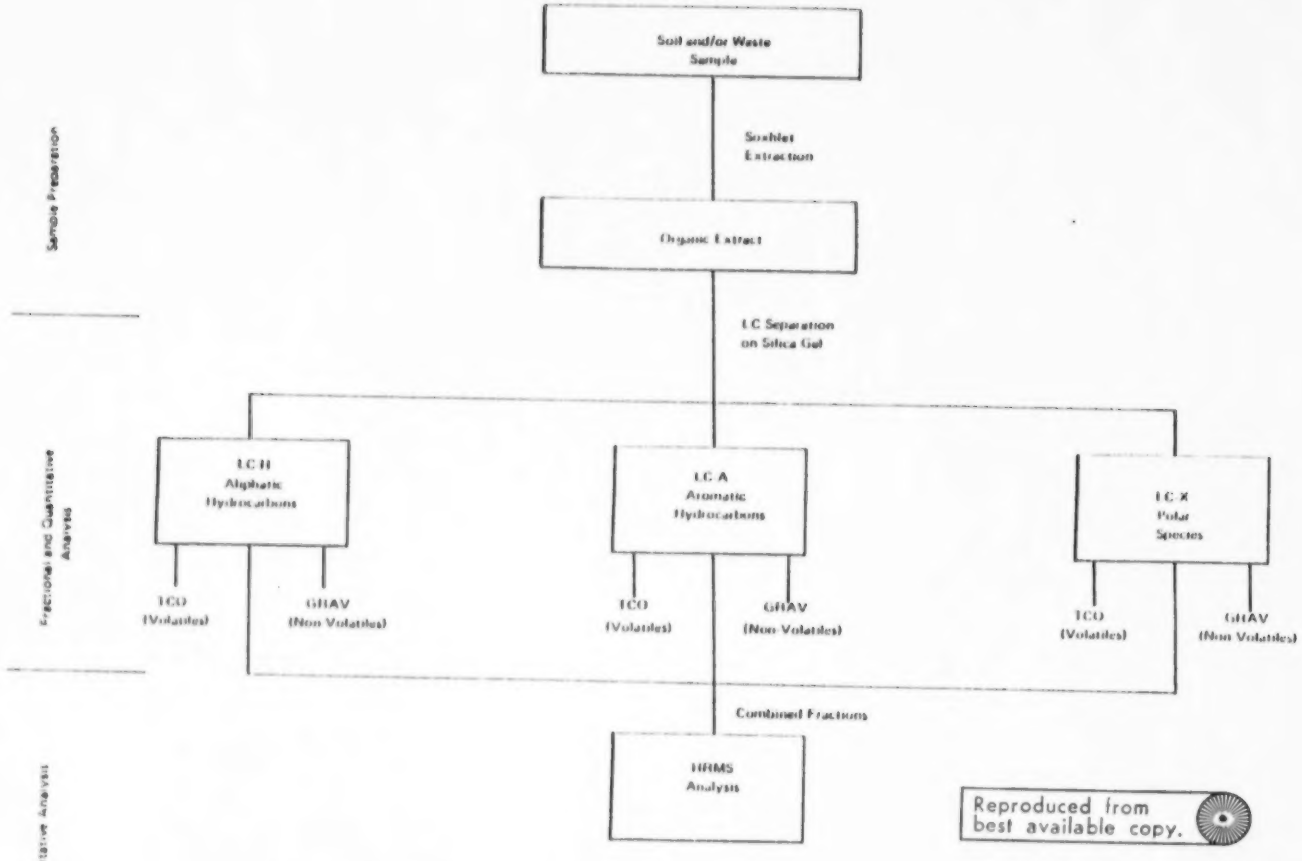

FIGURE 6. FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1 mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 11.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 11. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

Sample	% Water	Dry Wt. Extracted (kg)	Extract TCO (mg)	Extract GRAV (mg)	Extract Total (mg)	Extract Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 7 .

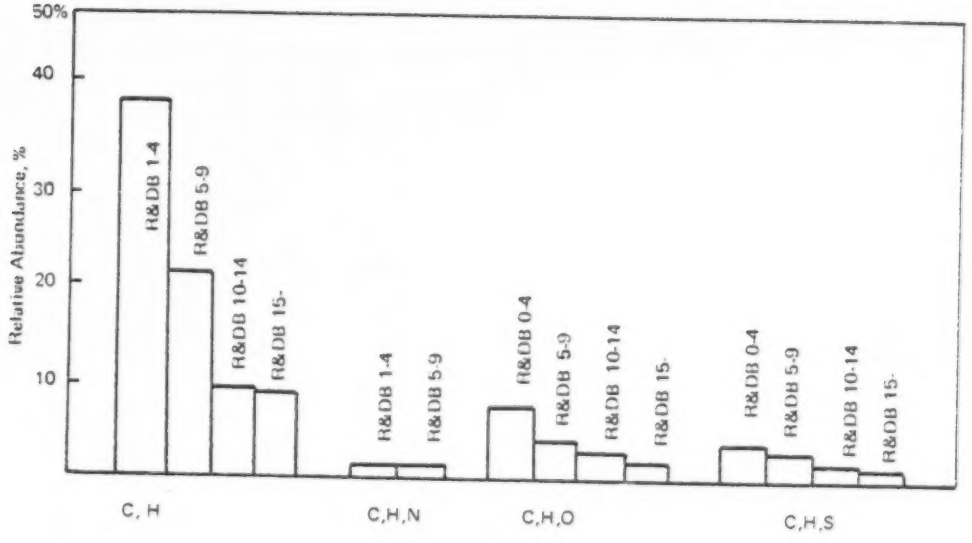

FIGURE 7. EXAMPLE OF DISPLAY OF R+DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT